

Development of Ceramic Foams Using Cast Iron Slag as a Raw Material

J. F. Lara-Sánchez^{*1}, H.F Lopez², M. Rodríguez-Reyes³, J. A. Díaz-Guillen⁴, J. R. Parga-Torres⁵

^{1,3,4,5}Instituto Tecnológico de Saltillo, Saltillo, Venustiano Carranza 2400, col Tecnológico C.P. 25269, Coahuila, México

²Materials Science and Engineering Department. University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53211, USA. hlopez@uwm.edu

^{*}jela413@gmail.com; ²hlopez@uwm.edu; ³mreyes@itsaltillo.edu.mx; ⁴jadiaz@itsaltillo.edu.mx;

⁵jrarga@itsaltillo.edu.mx.

Abstract

In this work experimental foams based on cast iron slag were made in order to investigate the potential application of cast iron slag (CIS) for the production of relatively economic high strength ceramic foams. The foams were processed using the slip cast method and as a base material $\text{Al}_2\text{O}_3\text{-SiO}_2$ with a systematic addition of CIS from 25 % all the way to foams consisting of 100 % CIS. After sintering at 1473 K (1200°C) for two hours quantitative and qualitative determinations indicated that as the amount of CIS was increased in the experimental foams, the dominant phases formed were anorthite, pseudowollastonite and sillimanite. Determinations of the exhibited pore size and percent porosity indicated that the maximum values were found in the foams containing up of 100 % CIS. In addition, the density of the high CIS foams was reduced significantly (down to 1.8 g/cm³) as a result of the increased porosity. This was accompanied by a high compressive strength of the order of 16 MPa for the high CIS foams. Apparently, the combination of phases developed during foam sintering in the high CIS provide significant strength to the porous foam material.

Keywords

Ceramic Foams; Slag Cast Iron; Slip Casting; Compressive Foam Strength

Introduction

Ceramic foams are porous materials, with unique properties for applications as liquid metal filters in foundries, thermal insulation, catalytic supports, gas filters, and other applications. Among the desirable properties of ceramic foams are a high melting point, low thermal conductivity, high specific surface, resistance to chemical attack, a low dielectric constant and a low density combined with high strength [1]. Moreover, the distribution, shape and size of the exhibited porosity is of outmost importance as it is determinant for the exhibited fluid permeability properties. The porosity type in ceramic foams can either be open, close or interconnected, with open porosity being highly desirable as it retains a high surface area which is characterized by an excellent permeability [2].

There are various methods available for producing ceramic foams which include replica, sol gel, direct foaming, gel casting, and slip casting [2-4]. In general, a set of sacrificial polymeric particles are employed, which are subsequently eliminated during the thermal treatment leading to the porous structure. Among the processing methods, slip casting is an economic method in making ceramic foams with pore sizes between 100 and 200 μm , and approximately 40 to 90 % of ceramic material in the foam [2, 5, 6]. Nevertheless, some of the properties of ceramic foams can be negatively influenced by increasing porosity such as the mechanical integrity.

Typically, ceramic foams are made of alumina or alumina-silica compounds. In the case of alumina foams they are widely used in aluminum melt filtration to remove oxide and other impurities [7]. However, alumina foams are relatively weak with compressive strengths reaching typically less than 1 MPa particularly as the porosity content is relatively high [8]. In addition, these ceramic foams can be relatively expensive making alternative raw materials such as foundry slags and other slags an attractive material in processing ceramic foams. Metallurgical slags are a

byproduct of metal processing and currently they have no further use in industrial applications. As a result, there are vast amounts of metal slags that can be considered as inexpensive raw materials for ceramic foam production.

According to the World Steel Association, the steel production in the world in April of 2015 was 135 Mt [9]. Assuming that the amount of slag produced as a byproduct is roughly one fourth of the steel production [10, 11], 35 Mt of slag are also produced which do not have any important applications. Most of this slag remains in large industrial backyards with only a small portion being used in the cement industry. As the world continues to increase the production levels of iron and steel, slag transportation, yard storage and soil contamination will continue to be highly critical factors that need to be satisfactorily addressed.

There have been significant efforts in investigating potential applications and use of slags in various ways; (a) as a replacement material in the cement industry [12]; (b) as an aggregate in construction materials such as concrete [13, 14] and (c) as abrasive materials, particularly in SiO₂ rich slags after thermal processing to enhance the slag hardness [15]. Other works have considered the use of cupola slags in processing porous materials such as zeolites for hydrogenation of aromatic hydrocarbons, including CO₂ as they are SiO₂ rich amorphous materials [16].

As mentioned before, in the fabrication of ceramic foams the most popular materials are Al₂O₃, SiO₂, SiC, Na₂SiO₃ and Al₂O₃SiO₂. Hence, in this work a novel application is proposed which considers foundry slags as a viable alternative to the production of alumina based ceramic foams. In the particular case of iron foundries, cupola slags are dominant in silica with typical chemical compositions in wt. % of: SiO₂ (47%), CaO (24%), Al₂O₃ (12%), MgO (9%), Fe₂O₃ (5%). Other compounds such as Na₂O, K₂O, TiO₂, MnO are also present but in relatively small amounts (less than 1 %). Hence, a potentially attractive ceramic filter for molten iron would be a ceramic material which will have a high resistance to molten metal attack such as one made up of cast iron slag.

In this work the slip casting method was used to produce ceramic foams with increasing contents of foundry slag starting from a 58 % Al₂O₃/42 % SiO₂ mixture, all the way to pure cast iron slag (CIS). In particular, the role of the cast iron slag on the pore microstructure and exhibited physical and mechanical properties of the processed ceramic foams was investigated.

Experimental Procedure

Materials

In this work alpha alumina (α -Al₂O₃ Sasol, 2.8 μ m particle size), silica (SiO₂ Merck, 28 μ m particle size), cast iron slag (CIS) of chemical composition (in wt. %): 5% Al₂O₃, 38% SiO₂, 49% CaO, 2% MnO, 2% Fe₂O₃, and 4% other, were employed as raw materials in processing ceramic foams of various compositions. In addition, polymethyl metacrylate (PMMA) was employed as the agent for pore generation and a suspension was made using poly-acrylic acid as a dispersant in a 35 % water solution containing dextrin and the binder agent (5% w.t., based on solid content).

Processing

The suspension was prepared using de-ionized water and stirring for five minutes at 200 RPM. The various ceramic compositions were introduced to the suspension together with the pore agent (PMMA 60% w.t.) in order to obtain a slurry. The slurry was then slip cast to obtain green ceramic foam samples. The green foams were then dried at 353 K (80°C) for 2h before firing them in a Thermolyne 4600 furnace. In the first heating stage the temperature was set at 873 K (600°C) for one hour in order to eliminate the pore agent, PMMA. This was followed by heating to 1473 K (1200°C) for 2h to induce sintering and thus produce the ceramic foams. In all the cases, the heating rate employed was 5 K/min. Afterwards, the ceramic foams were cooled to room temperature inside the furnace. Five different compositions were processed and they are given in Table 1. In particular, the starting foam R-0 had no cast iron slag (CIS) but it consisted of 42 % SiO₂ and 52 % Al₂O₃. The other foams contained the wt. % of the reference R-0 ceramic compounds (42 % SiO₂, 58 % Al₂O₃) as described in Table 1, with a systematic increase in the amount of CIS until the last one was fully made of CIS.

TABLE 1 SELECTED COMPOSITIONS FOR THE EXPERIMENTAL CERAMIC FOAMS

Foam	Wt. % ceramic content in experimental foams		
	58 % Al_2O_3	42 % SiO_2	CIS
R-0	100		0
R-25	75		25
R-50	50		50
R-75	25		75
R-100	0		100

Characterization Techniques

The apparent density of the experimental ceramic foams was determined using the Archimedes principle in 10 mm X 10 mm X 10 mm samples and using deionized water at room temperature. The exhibited morphology, distribution and pore size was then determined using a scanning electron microscope (SEM) JEOL JSM 6610LV. In addition, samples in powder form were used for X-Ray diffraction determinations of the present phases. In this case, an X ray diffractometer, Pert Phillips was used at 40 kV and 40 mA and a scanning rate of $2^\circ/\text{min}$ in the 2Θ scanning range of 10° to 70° . The mechanical strength of the ceramic foams was measured using a universal testing machine MST model QTEST/100 at a speed of 0.5 mm/min in cylindrical samples of 10 mm diameter by 20 mm in length.

Results and Discussion

Pore Morphology

Figure 1 shows ceramic foam cubes and corresponding porosity for the various compositions considered in this work. Notice that the exhibited porosity is strongly influenced by the ceramic foam composition as it leads to different pore sizes, shapes and interconnectivity. In general, it was found that both, the density of pores and the average pore size in the experimental ceramic foams tend to increase by increasing the wt. % CIS. Some porosity tends to be of spherical shape but it is typically irregular in morphology. In addition, it is apparent that there is an increase in pore interconnectivity in the high CIS foams (see Fig. 1e).

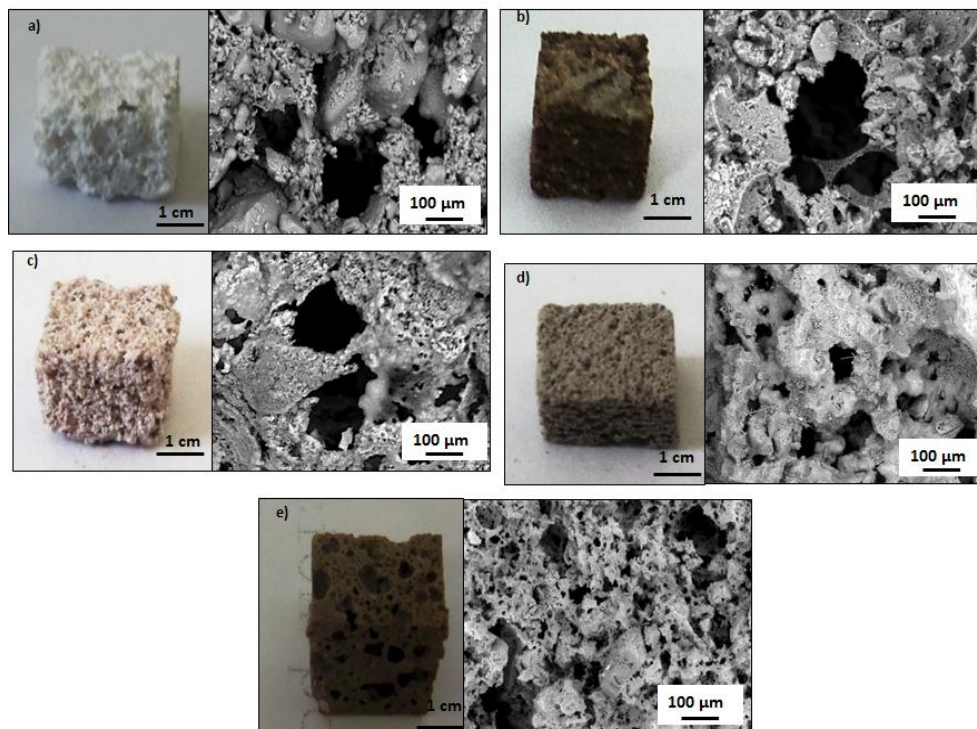


FIG. 1 SEM MACRO AND MICROGRAPHS OF THE VARIOUS CERAMIC FOAMS AFTER FIRING AT 1473 K (1200 °C). (a) R-0 (Al_2O_3 - SiO_2), (b) R-25 (75% Al_2O_3 - SiO_2 /25% SCI), (c) R-50 (50% Al_2O_3 - SiO_2 /50% SCI), (d) R-75 (25% Al_2O_3 - SiO_2 /75% SCI) and (e) R-100 (100%SCI).

Mapping of the various elements and the elemental distribution in these foams is shown in Figure 2. Notice from this figure that in the R0 and R25 ceramic foams O and Al are dominant, but there is some Si in the foams. As the CIS content increases (R50 to R100 foams) Ca is also detected in the experimental foams. Apparently, the Ca distribution is highly uniform and covers all of the area exposed. A similar effect is found for the Si distribution in the foams. As Ca and Si become part of the Ceramic foam composition it is expected that new phases have formed or introduced such as parawollastonite, sillimanite and anorthite as these compounds are typically found in foundry slags.

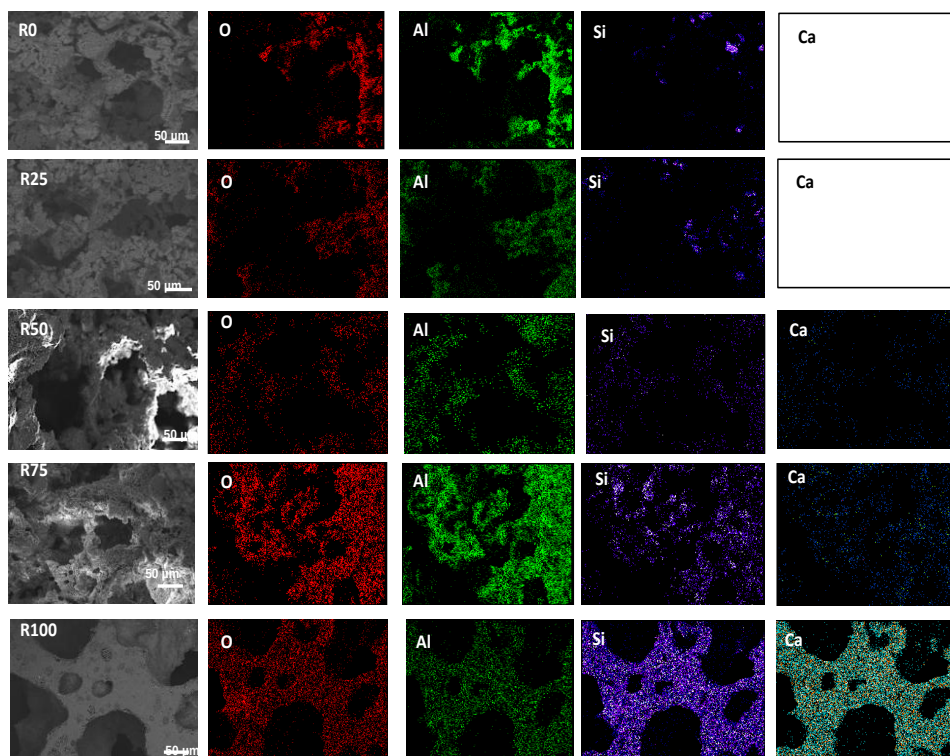


FIG. 2 SEM MAPPING OF ELEMENT DISTRIBUTION: O, Al, Si and Ca IN THE 5 EXPERIMENTAL FOAMS.

Compound Development

From X-ray diffraction determinations, various crystalline compounds were found to develop after firing at 1473 K (1200°C) as shown in Fig. 3. In the R-0 foams the phases identified are α - Al_2O_3 and SiO_2 . As CIS was added to the ceramic foams (samples R-25 to R-100), anorthite ($\text{Al}_2\text{CaSi}_2\text{O}_8$), sillimanite (Al_2SiO_5), parawollastonite (CaSiO_3) and lime (CaO) were found to be part of the resultant microstructure.

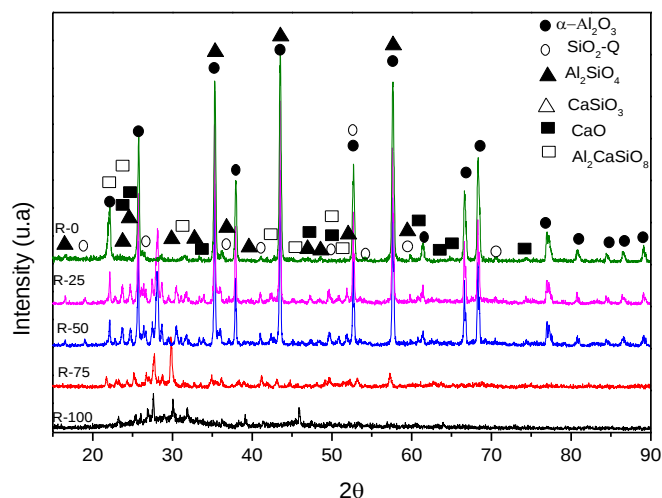


FIG. 3 X-RAY INTENSITY DIFFRACTION PEAKS CORRESPONDING TO THE EXPERIMENTAL CERAMIC FOAMS AFTER SINTERING AT 1473 K (1200°C) FOR 2 HOURS.

In addition, the relative amounts of the various phases developed in the experimental foams are schematically shown in Figure 4. Notice from this figure that as the amount of CIS is increased the amount of anorthite produced by reaction between alumina and parawollastonite (CaSiO_3) increases up to a maximum of 36.78 % (R-100 foam) concomitant with a maximum amount of parawollastonite (40.2 %). There are reports suggesting that the pseudowollastonite (CaSiO_3) phase forms due to reaction between CaO and SiO_2 at 1373 K (1100°C), and it can melt at 1533 K (1260°C) [15]. Also a maximum amount of sillimanite (Al_2SiO_5) of 11.98 % is present in the R-100 foams. In contrast the amount of silica (SiO_2) continually decreases and it is inexistent in the R-100 experimental foam. Except for the R-0, the amount of alumina remains relatively low and reaches a maximum of 6 % in the R-100 foam.

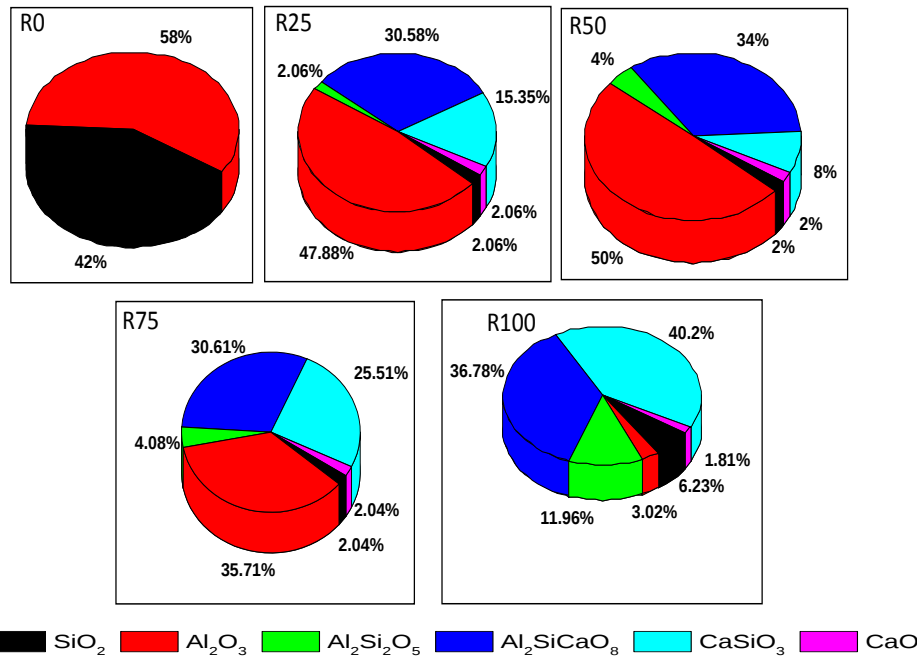


FIG. 4 MEASURED PHASE PERCENT IN THE EXPERIMENTAL FOAMS AFTER SINTERING AT 1473 K (1200°C) FOR 2 HOURS.

It is well known that at room temperature, pseudowollastonite (CaSiO_3) and anorthite ($\text{Al}_2\text{CaSi}_2\text{O}_8$), both exhibit little contraction and good resistance to thermal shock combined with a low coefficient of thermal expansion [17, 18], which make the R-100 experimental foam highly attractive for processing foams from cast iron slags. Figure 5 shows the effect of sintering and CIS composition on the amounts of exhibited phases in the experimental foams.

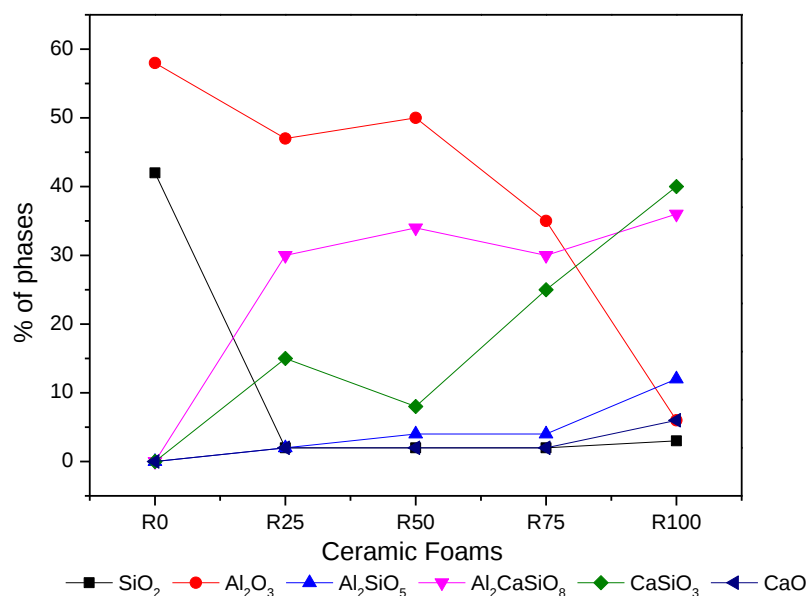


FIG. 5 GRAPHIC PLOT OF PHASE PERCENT FOR THE VARIOUS EXPERIMENTAL FOAMS AFTER SINTERING AT 1473 K (1200°C) FOR 2 HOURS.

A determination of the size and distribution of the exhibited porosity indicated that the average pores size for the R-0 and R-50 foams was of the order of 52 to 55 μm . As the amount of CIS is increased the average pore sizes increase up to 66-76 μm in the R-75 and R-100, respectively (see Figure 6).

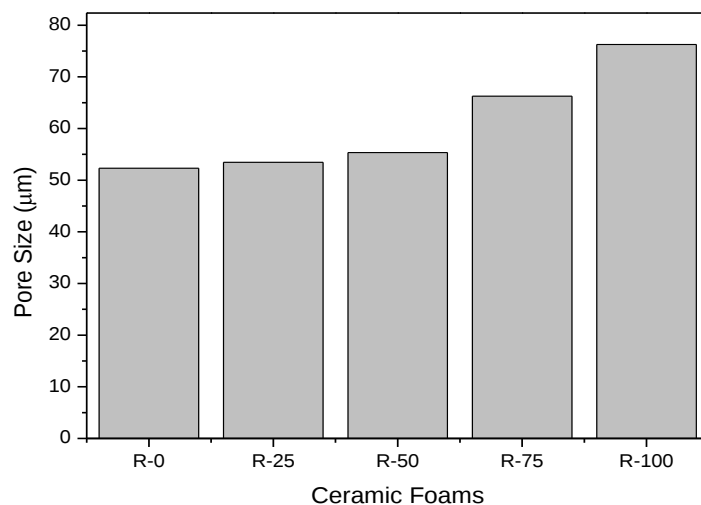


FIG. 6 HISTOGRAM SHOWING PORE SIZE DETERMINATIONS IN THE VARIOUS EXPERIMENTAL FOAMS AFTER SINTERING AT 1473 K (1200°C) FOR TWO HOURS.

The percent porosity in the experimental foams after sintering is shown in Figure 6. Notice the tendency to a reduced porosity which reaches a minimum in the foams with the addition of CIS all the way to R-50. Beyond this CIS content, the amount of porosity increases up to 55 %. This figure also shows that the minimal amount of porosity corresponds to the highest relative foam density (0.95). It is well known that [10] cast iron slags are prone to generate porosity in a spontaneous way due to the different compounds that are formed during the slag development. This fact and also the addition of PMMA nodules as a pore agent can explain the relative high porosity volume fractions exhibited in the high CIS experimental foams.

Physical and Mechanical Properties

The density determinations of the experimental foams sintered at 1473 K (1200°C) are shown in Figure 8. It is found that by increasing the slag content, the exhibited density increased up to a maximum for the foam R-50. Then, it is reduced to values below the one corresponding to the R-0 foams (i.e. from 2.28 g/cm³ down to 1.32 g/cm³, see also Fig. 7). The density results are a combination of pore volume fraction and present phases, with porosity becoming the dominant component in the high CIS foam (R-100).

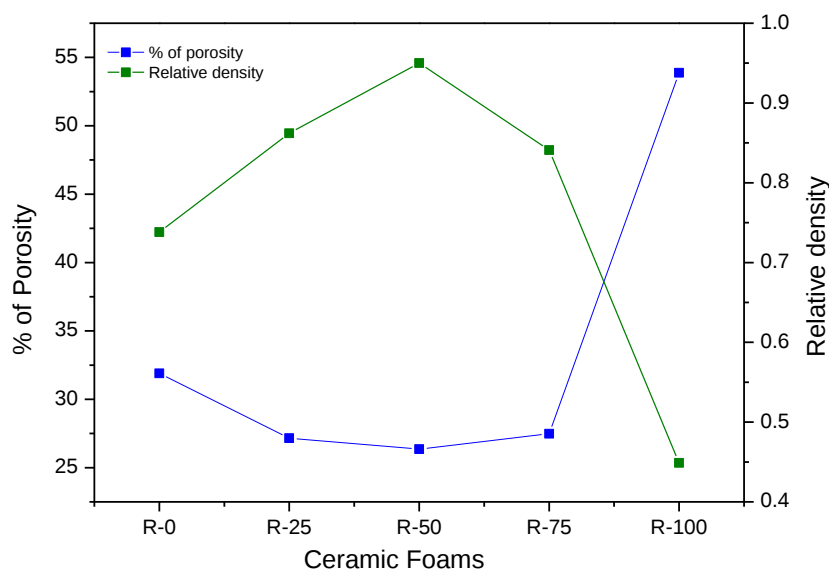


FIG. 7 PERCENT POROSITY AND RELATIVE DENSITY AS A FUNCTION OF THE CIS CONTENT IN THE VARIOUS FOAMS (R0, R25, R50, R75, R 100).

Figure 8 shows the exhibited compressive strength for the experimental foams. Notice that the compressive strength tends to increase beyond the values found for the R-0 and R-25 (1MPa), with the content of CIS. A maximum is reached in the R-100 foam with values of up to 16 MPa. The exhibited strength of the R-75 and R-100 foams is comparable with the one reported by [19] on Si₃N₄. In their work, they employed an inert gas (N₂) atmosphere and high sintering temperatures (1973 K). The ceramic foams obtained had a compressive resistance 9 to 14 MPa. Nevertheless, this process is expensive and not as simple when compared with the one employed in this work.

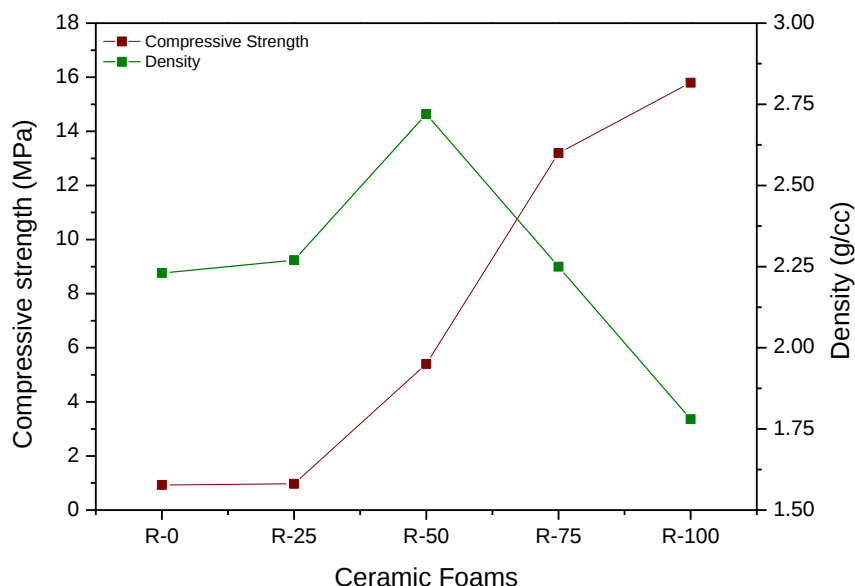


FIG. 8 DENSITY AND COMPRESSIVE STRENGTH AS A FUNCTION OF THE CIS CONTENT IN THE VARIOUS FOAMS (R0, R25, R50, R75, R 100).

In general, in ceramic foams there are still various limitations such as brittleness, lack of pore control including strategies for submicron porosity including an absence of models that relate pore structure to mechanical properties. Nevertheless, the exhibited compressive strength in the experimental foams can be satisfactorily described from the work of Ashby et co-workers [20]. In their work, a wide range of mechanical properties for foamed materials are related to an expression of the type:

$$\left(\frac{s^*}{s}\right) = c \left(\frac{\rho}{\rho_0}\right)^n = c(\rho_{rel})^n = c(1 - P)^n \quad (1)$$

where s^* is a mechanical property of the foam such as stiffness, elastic collapse stress, plastic collapse stress, crushing strength, or fracture toughness, s , is the corresponding mechanical property of the solid ceramic, ρ is the foam density, ρ_0 is the ceramic pore wall density, ρ_{rel} is the (ρ/ρ_0) ratio, P is the fraction of foam porosity, c is a geometric material constant and n is an exponent whose value is 2 for closed-cell foams and 3/2 for open-cell foams.

From the above expression, it is clearly evident that the foam mechanical properties are primarily dependent on the corresponding foam material properties and on the relative foam density. In the present work, the foam material composition is modified for each of the experimental foams. Hence, the foam properties vary from R-0 to the R-100 foams. In particular, notice that for the case of the R-100 foam, which exhibits a compressive or crushing strength $s^* = \sigma^*$ of 16 MPa. Assuming open-cell foams which are the largest foam class, and a constant $c = 0.65$ [20], the estimated compressive strength of the ceramic foam cell walls is 82 MPa. Since most ceramic foams exhibit relatively poor compressive strength ([7], the estimated compressive strength is highly attractive for the design of high strength, porous ceramic foams. In this particular case, the inherent compressive strength is likely to be associated with the formation of the dominant phases anorthite and parawollastonite and to some extent the presence of sillimanite (see Fig. 4). According to the literature, these compounds possess relatively high mechanical properties such as compressive strength and toughness [11, 12, 21].

From this work, it is evident that it is plausible to economically process ceramic foams with a high strength and a relatively low density using cast iron slag which currently does not have any important industrial application. In

this work, it is apparent that foams with high CIS contents (R-75 and R-100) can be significantly strong (up to 16 MPa compressive strength). Considering the relatively high porosity exhibited in these porous materials particularly the R-100, these foams are highly attractive to be considered for potential applications for molten iron filtration. Moreover, they are relatively inexpensive to process when compared with other currently available ceramic foams.

Conclusions

In this study using a simple process is employed for processing ceramic foams using cast iron slag (CIS) as a raw material and PMMA as a pore forming agent. Phase determinations in the sintered foams indicate that anorthite, sillimanite and pseudowollastonite become the dominant phases when the amount of added CIS increases all the way to 100 %. Density results indicate it falls down to values of 1.32 g/cm³ in experimental foams containing only SCI. In addition, porosity density reaches a maximum of 55 % including an increase in pore size in the high SCI foams. Finally, the compressive strength of the high SCI foam attains values of up to 16 MPa which makes it highly competitive with foams processed by relatively expensive techniques.

REFERENCES

- [1] H. Kim, S. Lee, Y. Hann and H. Park,. Control of pore size in ceramic foams: Influence of surfactant concentration. *Mats Chem & Phys.* 113, (2009), 441-444.
- [2] Y. H. Koh, E. J. Lee, B. H. Yoon and H.E. Kim, Effect of polystyrene addition on freeze casting of ceramic/camphene slurry for ultra-high porosity ceramics with aligned pore channels. *J. ACerS*, 89, (2006). 12, 3646-3653.
- [3] L. Andersson and L. Bergstrom, Gas-filled microspheres as an expandable sacrificial template for direct casting of complex-shaped macroporous ceramics. *J. ECerS.*, 28, (2008) 2815-2821.
- [4] K. Prabhakaran, A. Melkeri, N. Gokhale and S. Sharman, Preparation of macroporous alumina ceramics using wheat particles as gelling and pore forming agent, *Ceramic Int.* 33, (2007), 77-81.
- [5] P. Sepulveda, Gelcasting foams for porous ceramics, *Bull. ACerS*, 76, (1997), 61-65.
- [6] S. Luyent, J. Mullens, A. M. Coymas, I De Wilde, I. Thisj and R. Kemps, Different methods to synthesize ceramic foams, *J. ECerS*. 29, (2009), 829-832.
- [7] Y. Han, J. Li, Q. Wei and K. Tang, The effect of sintering temperatures on alumina foam strength, *Ceramic Int.*, 28, (2002), 755-759.
- [8] R. Brezny and D. J. Green, Fracture behavior of open-cell ceramics, *J. ACerSoc.*, 72, (1989), 1145-1152.
- [9] www.worldsteel.org
- [10] I. Pontsont and E. Bernardo, Self-glazed glass ceramic foams for metallurgical slag and recycled glass. *J. Cleaner Prod.*, 59, (2013), 245-250.
- [11] M. Singh and R. Siddique, Compressive strength, drying shrinkage and chemical resistance of concrete incorporating coal bottom ash as partial or total replace of sand. *Const. & Bldg. Mats.* 68, (2014), 39-48.
- [12] M. R. F. Gonçalves, C. K. Fillipeto, J. Viceni and C. P. Bergmann, 2011. Evaluation of mechanical performance of cement matrix composites with dispersed phases used in substitution to asbestos. *Const. & Bldg. Mats.* 25, (2011), 320-327.
- [13] V. P. Sukhorukov, Composition and conditions of formation of andalusite-kyanite-sillimanite pegmatoid segregations in metamorphic rocks of the Tsel block. *Russian Geology and Geophysics.* 48, (2007), 478-482.
- [14] S. Rahman, U. Feustel and S. Freimann, Structure description of the thermic phase transformation sillimanite-mullita. *J. ECerS*, 21,(2001), 2471-2478.
- [15] R. Anuwattan and P. Khummongkol, Conventional hydrothermal synthesis of Na-A zeolite from cupola slag and aluminium sludge. *J. Hazardous Mats.*, 166, (2009) 227-232.
- [16] T. Zhang, Q. Yu, J. Wei, J. Li and P. Zhang, Preparation of high performance blended cements and reclamtion of iron concentrat for basic oxygen furnace Steel slag. *Resources, Conservation and Recycling.* 55, (2011) 48-55.

- [17] S. Ji, E. Rybacki, R. Wirth, Z. Jaing and B. Xia, 2005. Mechanical and Microstructural characterization of calcium aluminosilicate (CAS) and SiO₂/CAS composites deformed at high temperature and high pressure. *J. ECerS.*, 25, (2005), 301-311.
- [18] A. A. Jara, S. Goldberg and M. L. Mora, Studies of the surface charge of amorphous aluminosilicates using surface complexation models. *Journal of Colloid and Interface Science.* 292, (2005), 160–170.
- [19] L. Y. Yin, X. G. Zhou, J. S. Yu, H. L. Wang, S. Zhao, Z. Luo and B. Yang B, 2013. Preparation of Si₃N₄ ceramic foams by simultaneously using egg white protein and fish collagen. *Ceram. Int.*, 39, (2013), 445-448.
- [20] K. Maiti, M. F. Ashby and L. S. Gibson, Fracture toughness of brittle cellular solids, *Scripta Metall.* 18, (1984), 213-217.
- [20] V. Dey, R. Kachala, A. Bonakdar and B. Mobasher, Mechanical properties of micro and sub-micron wollastonite fibers in cementitious composites. 82, (2015), 351-359.